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(71) Applicant *(for all designated States except US)*: HICKSON INTERNATIONAL PLC [GB/GB]; Wheldon Road, Castleford, West Yorkshire WF10 2JT (GB).

(72) Inventors; and
(75) Inventors/Applicants *(for US only)*: CORNFIELD, Judith, Ann [GB/GB]; 3 Redhill Mount, Castleford, West Yorkshire WF10 3AE (GB). RYAN, Neil, Patrick [GB/GB]; 22 Fairfield Way, Tadcaster, North Yorkshire LS24 9SP (GB). WALKER, David [GB/GB]; 45 Park View, Townville, Castleford, West Yorkshire WF10 3HZ (GB).

(74) Agent: WOODMAN, Derek; Frank B. Dehn & Co., 179 Queen Victoria Street, London EC4V 4EL (GB).

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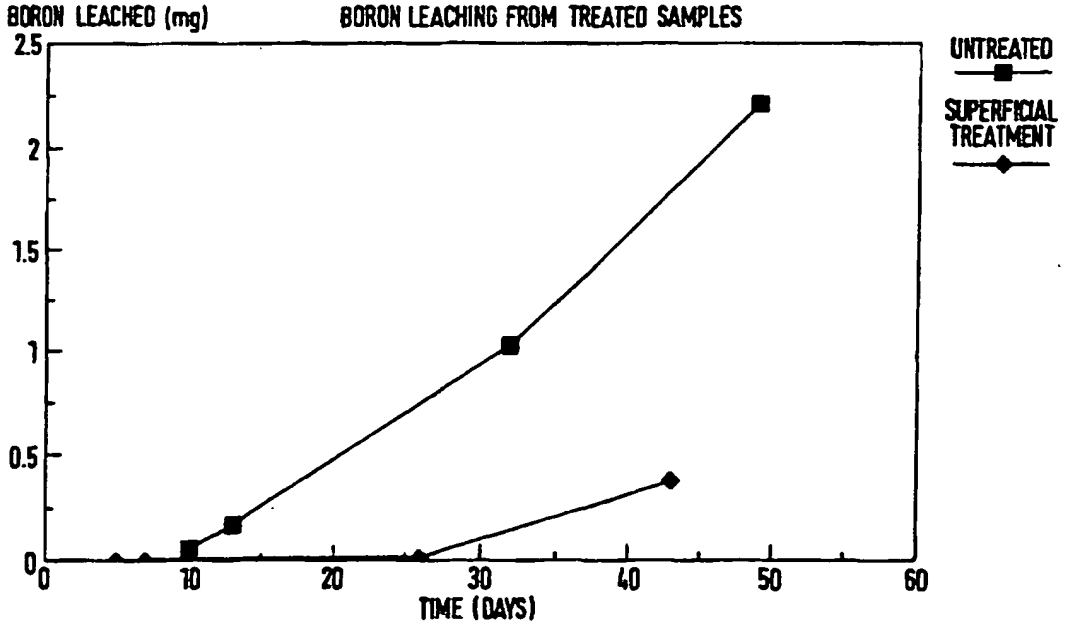

(57) Abstract

This invention relates to methods of preserving a substrate which comprise applying to the surface of the substrate a biocide and a polymeric compound and implanting into the substrate a preservative composition comprising a water diffusible biocide. Substrates, in particular wood and other solid cellulosic material which have undergone this treatment are also described.

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Method for preserving wood and other substrates

This application relates to a method for preserving wood and other substrates, and to kits for use in such methods.

Numerous methods of applying a wood preservative to wood are known and the choice of application method depends primarily on the type of preservative (eg solid, liquid or gaseous state, waterbased or solvent based) and the subsequent hazard to which the treated wood will be exposed. For example if treated timber is to be used in a high hazard situation such as ground contact, a preservative applied by a penetrating process (pressure impregnation) is preferred, so that as much of the susceptible timber as possible is treated with preservative and hence protected against attack by microorganisms. For less hazardous situations such as external joinery, treatment using a partially penetrating process is preferred. The resulting preservative envelope, surrounding an untreated core, provides a protective barrier against wood destroying fungi.

The physical and chemical nature of wood causes it to shrink and swell as the moisture content changes. This can often be an undesirable property of wood, especially in applications where machining tolerances are small or the aesthetic properties of wood are important such as with external joinery. An increase in moisture content may cause window frames to distort or check, coating films can be damaged due to dimensional instability and grain raising can occur, resulting in an uneven timber surface. All of these problems have resulted in the preference for using organic solvent based preservatives

to treat external joinery. These preservatives will not cause the timber to swell or distort and the use of solvent allows the treated wood to be used more quickly than if waterbased treatments are used, due to the faster drying time. Organic solvent based preservatives are, however, far more expensive than water based products.

Superficial application of waterbased preservatives to timber will reduce the amount of water in the wood and will therefore reduce the problems of distortion and drying. However penetration of these preservatives is usually less than 3mm into the lateral face and so it is unlikely that this type of treatment will afford the same level of protection as a partially penetrating process where the penetration is typically 3-6mm into the lateral face. Superficial treatment of external joinery is therefore not widely practised and penetrating processes are preferred.

Water diffusible biocides are widely used to treat external joinery components. This technology is based on inserting solid implants of the diffusible biocide into the timber and is usually carried out as part of a remedial treatment process as opposed to pre-treatment during manufacture. This technology relies on the fact that when the timber becomes wet and the risk of decay increases, the biocide will be mobilised and prevent any subsequent attack by decay organisms. As long as the timber remains dry, (below about 20% moisture content) there is no significant risk of decay and the biocide will remain in its immobilised state. The primary disadvantage of such systems is that being water diffusible, the biocides will be susceptible to leaching from the wood, and will therefore be gradually depleted until the amount of biocide in the wood is insufficient

to prevent fungal decay. Another drawback is the fact that a moisture gradient may exist throughout the cross section of a timber component, with the centre often being at a lower moisture content than the surface. In this situation, the biocide would not be mobilised from the centre of the section and could therefore leave the surface of the timber susceptible to fungal degrade. This is especially important with joinery where the surface appearance is important and disfigurement by bluestain and other fungi is particularly undesirable.

According to one aspect of the invention, there is provided a method of preserving a substrate as herein defined which comprises applying to the surface of the substrate a biocide and a polymeric compound and implanting into the substrate a preservative composition comprising a water diffusible biocide.

It will be understood that the biocide and polymeric compound may be applied to the surface in the form of separate compositions, one comprising the biocide, and the other comprising the polymeric compound, but preferably they are applied in the form of a single, surface-applied preservative composition comprising both the biocide and the polymeric compound. For convenience, the invention will be discussed below with reference to methods wherein the surface treatment is applied in the form of a single surface-applied preservative composition comprising the biocide and the polymeric compound, but it will be understood that preferred features of this surface-applied composition discussed below are also applicable, where relevant to methods wherein the surface treatment is applied in the form of two separate compositions.

The preservative compositions used in the method of the

invention may be used to treat substrates such as wood or other solid cellulosic materials (such as medium density fibre board and other composite products). For convenience, the invention will be described hereinafter with reference to the treatment of wood but it will be appreciated that other materials may be treated analogously.

It has been found that in wood treated using the method of the invention there is surprisingly little leaching of the water-soluble biocide present in the implanted preservative composition when the wood is in contact with water. The reduction in leaching is observed even when the wood is exposed to severe conditions, for example, by immersion in water. It has also been found that the combination of the two preservative compositions used in the method of the invention results in excellent protection of the treated wood throughout its thickness. The surface-applied preservative composition protects the timber from attack by organisms such as bluestain fungi and mould and also serves to provide a barrier against invasion by decay fungi. If the timber does not reach a sufficiently high moisture content to solubilise the diffusible biocide in the implanted preservative composition, the surface-applied preservative composition affords protection until the diffusible biocide is solubilised and has diffused into the susceptible areas of the wood. When the moisture content of the timber eventually increases, the water diffusible biocide is solubilised and provides protection against fungal attack. The combination of treatments used in the method of the invention results in far better overall protection of the wood than would be expected from the results obtained when wood is treated with either form of preservative composition alone.

The method of the invention is particularly suitable for the treatment of external joinery (such as window and door frames) and overcomes all of the disadvantages of the known treatments of such products. Preferably the method is applied to treat joinery components before they are used in construction, rather than as a remedial treatment after decay has already occurred. This enables the application of the surface-applied composition to all surfaces of the component so that a substantially complete protective envelope around the component is formed. The method may also be used for the protection of timber to be exposed externally in, or out of ground contact or used in the construction of buildings.

In the method of the invention the various treatments may be applied in any order, for example, the surface-applied preservative composition may be applied before the composition comprising the water-diffusible biocide is implanted into the wood, or these two treatment steps may be reversed.

The implanted preservative composition is preferably in the form of a solid implant or paste. The water diffusible biocide must be of sufficient solubility in water to enable diffusion of the biocide through the wood when the wood becomes moist and vulnerable to decay. Suitable biocides include fungicidal or insecticidal compounds such as boric acid and other boron-containing compounds that have suitable water solubility such as disodium octoborate tetrahydrate; fluorides and silicafluorides; MBT (methyl-bis thiocyanate), polyhalogenated phenols such as pentachlorophenol or tribromophenol and their alkali metal or ammonium salts; quaternary ammonium salts and tertiary amine salts such as didecyl dimethyl ammonium

chloride, octyl decyl dimethyl ammonium chloride, dodecyl dimethyl benzyl ammonium chloride, dodecyl benzyl trimethyl ammonium chloride, dodecyl dimethyl amine acetate, didodecyl methyl amine chloride; isothiazolone derivatives such as 4,5-dichloro-2-(n-octyl)-4-isothiazolone-3-one or 2-methyl-4-isothiazolin-3-one, 2n-octyl-4-isothiazolin-3-one and mixtures of these and other related compounds. The solid implants may be prepared, for example, by conventional methods eg. by mixing together the biocide(s) and any inert ingredients to form a paste and then extruding the paste.

Particularly preferred water diffusible biocides are boron-containing compounds and fluorides. Disodium octoborate tetrahydrate and sodium fluoride are especially preferred.

The surface-applied composition is preferably an aqueous composition but it may instead contain one or more organic solvents, or it may contain both water and one or more organic solvents.

The polymeric compound in the surface-applied preservative composition is preferably a water-soluble or water-emulsifiable compound. The term "polymeric compound" includes, for example, compounds preparable by a polymerisation reaction and which contain at least 3 recurring units (monomers) per molecule, as well as resins, in particular, naturally occurring resins which have optionally been modified eg. modified linseed oil. Preferred polymeric compounds cure or set on drying by means of cross-linking reactions. Preferred polymeric compounds act as emulsifiers and may serve to solubilise any water insoluble biocides or act as a carrier for any soluble biocides present in the composition. The

polymeric compound may also improve the paintability characteristics of the treated wood. By way of example only, the following water soluble or water-emulsifiable polymeric compounds, or mixtures thereof may be present in the surface-applied composition: alkyds, modified alkyds, acrylics, polyvinyl acetate and derivatives thereof, modified linseed oil, polyurethane, epoxy and other suitable water soluble or water-emulsifiable resins or polymers. By "water-emulsifiable polymeric compound" is meant a polymeric compound capable of forming an emulsion when mixed with water and, if necessary, an emulsifier.

The amount of polymeric compound in the surface-applied composition is preferably kept to a minimum and ideally the composition contains insufficient polymeric compound to form a film on the surface of the treated wood. Preferably the composition contains less than 25%, and particularly preferably less than 10% by weight of polymeric compound. Preferably the surface-applied composition is a non-decorative composition, although decorative compositions (such as paint) may be applied after the wood has been treated according to the method of the invention.

The surface-applied preservative composition contains one or more biocides, for example, compounds having fungicidal or insecticidal activity, including eg. boric acid and other boron-containing compounds with sufficient water solubility and organic compounds that have useful activity against wood destroying fungi and insects. Such organic compounds include carboxylic acids such as napthenic acids and branched aliphatic acids and their metal salts such as copper and zinc napthenate; phenols and substituted phenols such as orthophenyl phenol and its alkali metal or ammonia

salts; polyhalogenated phenols such as pentachlorophenol or tribromophenol and their alkali metal or ammonium salts; quaternary ammonium salts and tertiary amine salts such as didecyl dimethyl ammonium chloride, octyl decyl dimethyl ammonium chloride, dodecyl dimethyl benzyl ammonium chloride, dodecyl benzyl trimethyl ammonium chloride, dodecyl dimethyl amine acetate, didodecyl methyl amine chloride; isothiazolone derivatives such as 4,5-dichloro-2-(n-octyl)-4-isothiazolone-3-one or 2-methyl-4-isothiazolin-3-one, 2n-octyl-4-isothiazolin-3-one and mixtures of these and other related compounds; sulphamide derivatives such as N,N-dimethyl-N-phenyl(N-fluorodichloro-methylthio)-sulphamide, N,N-dimethyl-N-toly-N-(dichlorofluro methylthio)-sulphamide; triazole derivatives such as 1-[2-(2,4-dichlorophenyl)-1,3-dioxalan-2-yl)-methyl]-1H-1,2,4-triazole; TCMTB (2-thiocyanatomethylthio)-benzothiazole; MBT (methylene-bisthiocyanate); IPBC (3-iodo-2-propynyl-butyl-carbamate); carbendazim and chlorothalonil; α-(2-(4-chlorophenyl)ethyl)α-(1, 1 - dimethylethyl)1H-1,2,4 triazol-1-ethanol (tebuconazole) and N-nitrosohydroxyl-amines such as N-nitrosophenylhydroxylamine, and N-nitroso cyclohexylhydroxylamine, either as their metal salts or as metal chelates. Insecticides such as the synthetic pyrethroids; permethrin, cypermethrin, cyfluthrin and deltamethrin; organo-phosphorous, carbamate and chlorinated hydrocarbons such as lindane; may also be incorporated in the formulation.

Particularly preferred biocides for use in the surface-applied composition are triazole compounds such as tebuconazole and propiconazole, and IPBC (3-iodo-2-propynyl-butyl-carbamate).

The surface-applied preservative composition may

optionally contain additives conventionally employed in timber preservation such as water repellents, colour additives, viscosity modifiers, corrosion inhibitors, thickeners, emulsifiers, dryers or plasticizers.

The surface-applied composition may be prepared, for example, by bringing all of the components into admixture. The compositions may be solutions or oil-in-water emulsions or microemulsions where the composition is aqueous and the water-solubility of the biocides is too low to form solutions of the required strength. The composition may optionally be prepared in concentrated form intended for dilution immediately prior to use. Concentrated compositions preferably contain 25 to 95%, particularly preferably 30 to 85% by weight of the polymeric compound.

The surface-applied preservative composition may be applied to the surface of the wood by any suitable method such as by brushing, dipping, deluging, spraying, vacuumatic coating or by double vacuum and vacuum low pressure treatment. Preferably the treatment results in an average lateral preservative penetration of less than three millimetres.

The preservative composition comprising the water-diffusible biocide may be implanted into the wood by any convenient method. Preferably, where this composition is in the form of a solid implant, this is achieved by drilling a hole at suitable points in the wood to be treated, inserting the solid preservative and sealing the hole with a suitable filler or wooden plug. Where the end use of the wood is known, it may be possible to implant the composition at points which are known to be particularly susceptible to decay eg. where the wood is

to be used as a window sill, the composition can be implanted near to the joint area.

After treatment using the method of the invention, the wood may be coated with stains, paints, other coatings or left uncoated depending on the requirements of the end user.

Where the desired finished product consists of two or more sections of wood adhered together (eg. a joinery component, such as a window or door frame), the adhesive used optionally contains one or more biocidally active compounds to further protect the susceptible joint areas. The sections of wood may be adhered together before or after the surface-applied and implanted compositions have been applied to the wood or they may be adhered together between these two treatment steps. Adhesives used to join timber components may contain for example, the following compounds conventionally present in such adhesives; phenol formaldehyde, phenol resorcinol formaldehyde, urea formaldehyde, melamine formaldehyde, isocyanates eg. polymeric diphenylamine-diisocyanate and PVA (poly vinyl acetate). The adhesives may also contain one or more biocidal compounds, for example, any of the biocidal compounds which are stated above to be suitable for incorporation into the surface-applied composition.

According to a further aspect of the invention there is provided a kit which comprises a surface treatment comprising a biocide and a polymeric compound and a preservative composition comprising a water-diffusible biocide. As with the method described above, the surface treatment may be in the form of separate compositions, one comprising the biocide and the other comprising the polymeric compound, but is preferably in

the form of a single surface-applied preservative composition. In the kits of the invention, the composition(s) making up the surface treatment is/are optionally in concentrated form intended for dilution immediately prior to use. Optionally the kits further comprise an adhesive suitable for adhering wood, which adhesive contains a biocide. The kits are useful in the method of the invention and accordingly the preferred aspects discussed above in relation to the method are also applicable where relevant to the kits.

According to a still further aspect of the invention there is provided wood (and in particular, joinery components) or other solid cellulosic material whenever treated by a method according to the invention.

The following non-limiting Examples further illustrate the invention.

Examples

Example A

To illustrate the effect of reduced leaching of diffusible biocide, the following experiment is described: Scots pine (*Pinus sylvestris*) sapwood samples (2 x 2 x 20cm) were drilled centrally in the end-grain to a depth of 6cm. A 3 cm solid diffusible implant containing 124g/Kg boron present as 582g/Kg disodium octoborate tetrahydrate and 110g/Kg available fluorine present as 243g/Kg sodium fluoride, was inserted and the hole sealed with a 3cm long wooden dowel. Three replicates with rods inserted were then treated by applying 250mm Hg vacuum for 3 minutes, and 0.25 kgf cm^{-2} pressure for 10 minutes to achieve less than 3mm average penetration yielding a superficial application of a formulation containing 0.25% w/w Tebuconazole, 0.25% Propiconazole, 0.2% IPBC, 0.5% methyl dioxitol, 3.3% water soluble polymeric alkyd surfactant, 95.5% water. A further three replicates contained implants but were not treated with the preservative formulation.

After conditioning at ambient temperature for two weeks, the samples were placed in glass beakers containing 100ml of de-ionised water with the preservative implanted ends in contact with the water. The beakers were covered to prevent loss of liquid by evaporation. At regular intervals up to 50 days, the samples were removed, the remaining liquid weighed and a sample (1g) extracted for boron analysis. The samples were returned to the beakers and the volume of water was adjusted to its original volume. The quantity of boron in the extracted samples was analysed by ion exchange chromatography and results from the analysis are illustrated graphically in Figure 1.

It was apparent that there was a surprising difference in the boron content of the extracted liquid samples between the samples that had been treated with the surface-applied formulation and the samples that had received no treatment. This result indicates that the application has in some way significantly reduced the leaching of boron from the samples. The implications of this are also significant in that reduced leaching of the boron from the wood will inevitably lead to an increased service life of the treated timber.

The compositions disclosed in the Examples below may be used to treat wood by methods analogous to that described in Example A above or by any of the other methods described herein. Where adhesives are described these may be used for any necessary adhesion of sections of wood to produced the desired finished product.

EXAMPLE 1

A. Surface-applied composition (Ready to use solution)

	%w/w
Tebuconazole	0.25
Propiconazole	0.25
IBPC	0.2
Methyl Dioxitol	0.5
Antifoam	0.05
Water soluble polymeric alkyd surfactant	3.30
Water	95.45

B.Solid Implant:

Disodium octaborate tetrahydrate	58.2
Sodium Fluoride	11.0
Inert Ingredients	30.8

Example 2

A. Surface-applied composition (Ready to use solution)

	%w/w
Hexaconazole	0.25
2n-octyl-4-isothiazolin-3-one	0.2
IBPC	0.3
Antifoam	0.05
Water soluble polymeric alkyd surfactant	6.54
Paraffin Wax emulsion	1.00
Water	91.66

B. Solid Implant:

	%w/w
Disodium octoborate tetrahydrate	58.2
Methyl bis thiocyanate	2.5
Inert Ingredients	39.3

C. Adhesive

	%w/w
Poly Vinyl Acetate Adhesive	97.5
IPBC	0.5
Methyl Dioxitol	2.0

EXAMPLE 3

A. Surface-applied composition (Ready to use solution)

	%w/w
Azaconazole	0.25
Propiconazole	0.3
Boric Acid	0.8
Methyl Dioxitol	0.25

Antifoam	0.05
Cypermethrin	0.05
Water soluble acrylic copolymer	3.72
Water	94.58

B. Solid Implant:

	%w/w
Sodium Pentachlorophenol	80
Sodium Fluoride	11
Inert Ingredients	9.0

C. Adhesive

Poly Vinyl Acetate Adhesive	96.4
Propiconazole	0.4
IPBC	0.2
Methyl Dioxitol	3.0

EXAMPLE 4

A. Surface-applied composition (in concentrated form - to be diluted to between 5 and 25% by weight in water.

	%w/w
Tebuconazole	5.0
Propiconazole	5.0
IPBC	4.0
Antifoam	1.0
Water emulsifiable modified linseed oil	85.0

B. Solid Implant:

	%w/w
Disodium octoborate tetrahydrate	68.0
Anhydrous Disodium Octoborate	14.0
Inert Ingredients	18.0

EXAMPLE 5

A. Surface-applied composition (Ready to use solution)

	%w/w
Tebuconazole	0.25
Propiconazole	0.25
IBPC	0.2
Methyl Dioxitol	0.5
Antifoam	0.05
Water soluble modified polymeric alkyd surfactant	3.30
Water	95.45

This composition may be used, for example, in conjunction with the solid implants described in any one of Examples 1 to 4 or 6.

EXAMPLE 6

A. Surface-applied composition (in concentrated form - to be diluted to between 5 and 25% by weight in water.

	%w/w
Zinc Versatate	6. 0
Anionic/non-ionic emulsifiers	0.3
Antifoam	0.5
Cypermethrin	0.5
Water emulsifiable modified linseed	

oil	92.7

B. Solid Implant:

Didecyl dimethyl ammonium chloride (80% active)	62.0
Anhydrous Disodium Octoborate	11.0
Methyl bis thiocyanate	1.25
Inert Ingredients	25.75

C. Adhesive

	%w/w
Phenol formaldehyde resin	99. 1
IPBC	0.4
Permethrin	0.5

Claims

1. A method of preserving a substrate of wood or other cellulosic material which comprises applying to the surface of the substrate a biocide and a polymeric compound and implanting into the substrate a preservative composition comprising a water diffusible biocide.

2. A method as claimed in claim 1 wherein the polymeric compound and the surface biocide are applied in the form of a single composition.

3. A method as claimed in claim 1 or claim 2 wherein the implanted, water diffusible biocide is in the form of a solid implant or paste.

4. A method as claimed in any one of the preceding claims wherein the water diffusible biocide is a fungicidal or insecticidal compound selected from the group comprising boric acid and other boron-containing compounds that have suitable water solubility; fluorides and silicafluorides; MBT (methyl-bis thiocyanate); polyhalogenated phenols and their alkali metal or ammonium salts; quaternary ammonium salts; tertiary amine salts and isothiazolone derivatives.

5. A method as claimed in claim 4 wherein the water diffusible biocide is disodium octoborate tetrahydrate or sodium fluoride.

6. A method as claimed in any one of the preceding claims wherein the polymeric compound is a modified naturally occurring resin.

7. A method as claimed in any one of the preceding claims wherein the polymeric compound is selected from

the group comprising alkyds, modified alkyds, acrylics, polyvinyl acetate and derivatives thereof, modified linseed oil, polyurethane, epoxy and other suitable water soluble or water-emulsifiable resins or polymers.

8. A method as claimed in any one of the preceding claims wherein the surface biocide is a fungicidal or insecticidal compound selected from the group comprising boric acid and other boron-containing compounds with sufficient water solubility; carboxylic acids and their metal salts; phenols and substituted phenols and their alkali metal or ammonia salts; polyhalogenated phenols and their alkali metal or ammonium salts; quaternary ammonium salts and tertiary amine salts; isothiazolone derivatives; sulphamide derivatives; triazole derivatives; TCMTB (2-thiocyanatomethylthio)-benzothiazole; MBT (methylene-bisthiocyanate); IPBC (3-iodo-2-propynyl-butyl-carbamate); carbendazim and chlorothalonil; α-(2-(4-chlorophenyl)ethyl)α-(1, 1 - dimethylethyl)1H-1,2,4 triazol-1-ethanol (tebuconazole); N-nitrosohydroxyl-amines, either as their metal salts or as metal chelates; synthetic pyrethroids and organo-phosphorous, carbamate and chlorinated hydrocarbons.

9. A method as claimed in claim 8 wherein the surface biocide is tebuconazole, propiconazole or IPBC (3-iodo-2-propynyl-butyl-carbamate).

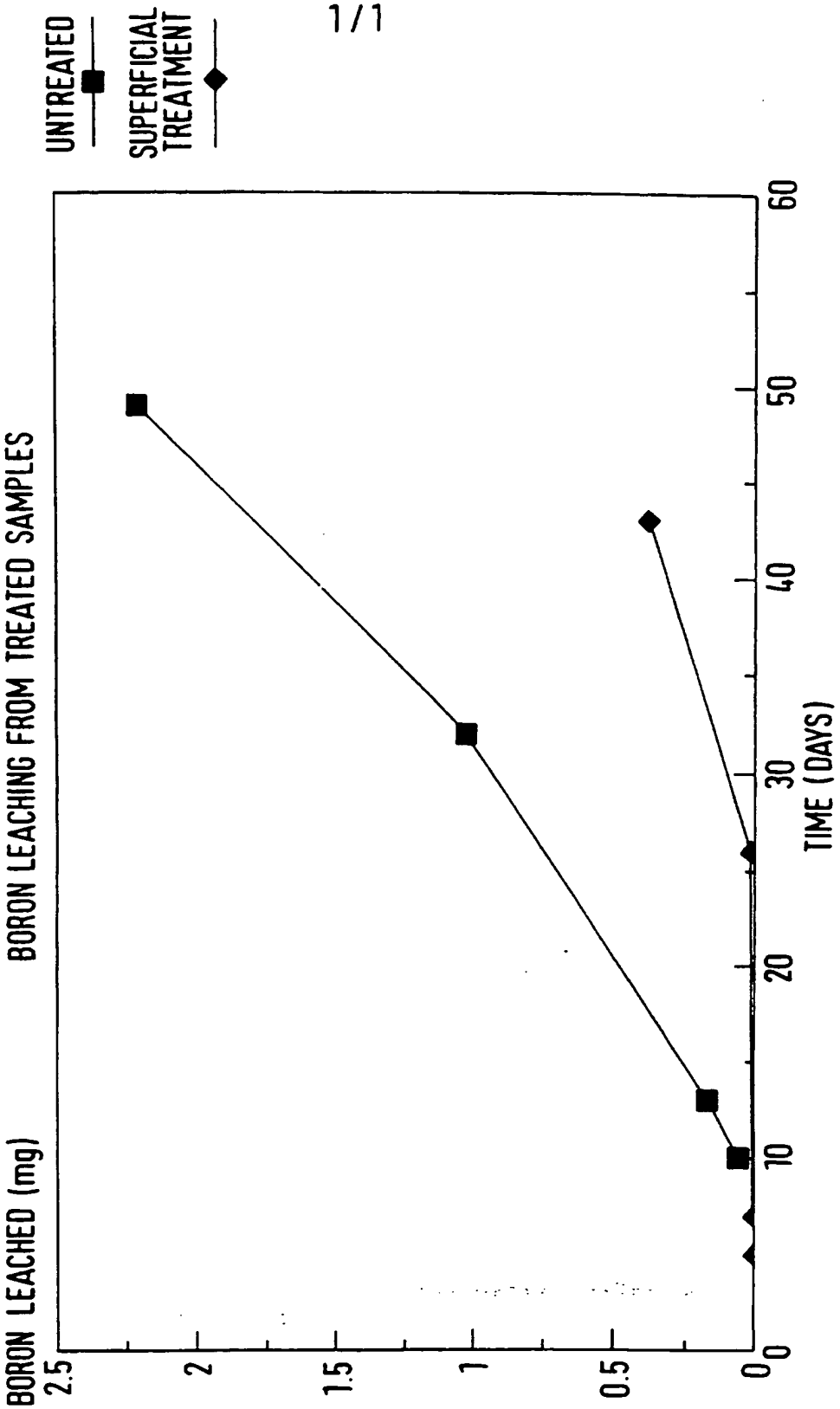
10. A method as claimed in any one of the preceding claims wherein the treatment to the surface of the substrate results in an average lateral preservative penetration of less than 3 millimetres.

11. A product containing (a) a surface treatment agent comprising a biocide and a polymeric compound and (b) a preservative composition comprising a water-diffusible biocide for simultaneous or sequential use in the

preservation of a substrate according to a method as claimed in any one of claims 1 to 10.

12. Wood or other solid cellulosic material which has been treated by a method according to any one of claims 1 to 10.

FIG. 1


BORON LEACHING FROM TREATED SAMPLES
UNTREATED
SUPERFICIAL TREATMENT
BORON LEACHED (mg)
2.5
2
1.5
1
0.5
0
0
10
20
30
40
50
60
TIME (DAYS)

INTERNATIONAL SEARCH REPORT

International Application No
PC[illegible]/GB 96/00511

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 B27K3/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 B27K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO,A,89 03287 (MANCHEM LTD) 20 April 1989 see claim 13 ---	1
A	WO,A,92 18007 (SANEISH PTY LTD) 29 October 1992 see page 8, line 7-11 ---	1
A	US,A,5 202 150 (BENSON DAVID K ET AL) 13 April 1993 ---	
A	US,A,5 083 408 (BLOM CORNELIS W ET AL) 28 January 1992 -----	

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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